

FULLPROF as a new tool for flipping ratio analysis: further improvements

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Abstract

In the international workshop on polarized neutron for condensed matter investigation (Jülich, September 2002), we presented the implementations done in FULLPROF in order to introduce the ability of performing flipping ratio analysis. During this year we have modified the program in order to extend the initial features. We have tested these new implementations by re-analyzing flipping ratio data on Metrz–Nit ($C_{10}H_{16}N_5O_2$) compound.

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1. Introduction

The spin moment of neutron interacts with the spin density of ions during scattering and diffraction processes. This makes neutrons as the most valuable magnetic probe to study the magnetism of solids at an atomic level. To larger exploit this ability, the knowledge of the initial (and the final) polarization direction of the scattering neutrons has been largely used. In this context, the measurements of flipping-ratio (FR) has been used

in a wide variety of scientific fields, to study the magnetization density of crystalline materials ranging from intermetallic compounds to transition metal oxides and organic compounds. The analysis of FR measurements, specially when the space group (SG) of the crystal structure is non-centrosymmetric, requires the use of computer programs that, sometimes, are difficult to use for non-specialized users. The final goal of the implementations done in FULLPROF was to create a easy-to-use tool that allows to non-specialized users to pay more attention in the physics behind the problem rather than in the practical difficulties of the analysis. This goal is achieved through the use of the PCR input-files that have a format familiar for many researchers using neutron–diffraction techniques. The use of FULLPROF for dealing with this has also the advantage

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that the same tool is able to analyze nuclear and FR data (at present, separately).

2. FULLPROF features and improvements for FR analysis

As is largely explained and detailed in Ref. [1], FULLPROF calculates the total magnetization density as the sum of monoatomic magnetization densities. Each monoatomic magnetization density can be modeled using two different approaches: the density or the orbital approximation. The density approximation consists on taking the angular part of the magnetization density as a development on real spherical harmonics [2] up to $l = 4$, while the radial part is taken as Slater-type functions. In the orbital approximation, the angular part of the magnetization density is taken as a pure p, d or f orbital or a s–p hybrid. In the first three cases, the radial part of the spin density can be taken from (i) the international tables of crystallography [3] (through the values of $\langle j_l(s) \rangle$) (ii) calculated through an hydrogen-like radial function and (iii) calculated as a Slater-type function. In the case of an hybrid the radial part must be calculated through an hydrogen-like radial function. In all the cases, the nuclear structure factor was calculated from the structural model provided in the PCR (input) file [4].

During the last year, we have introduced some changes that enlarge the possibilities that the program can handle. The first is that in the case of an hybrid s–p orbital, the radial function can also be chosen to be a Slater function. With this, the hybrid s–p orbital can also be used to analyze the case of an spherical s orbital with further possibilities to add to the radial function.

The other great change concerns the nuclear contribution to the structure factor that can be now read from the input files instead of being calculated from the details provided in the PCR file. This can help to simplify the PCR files, but in addition can be used to relax the monoatomic approximation and magnetization density out of the atomic positions can be easily introduced. It also helps to overcome the difficulty of having magnetic atoms with strongly anisotropic tem-

perature factors that, otherwise, must be taken as isotropic.

Not concerning the refinement of FR, we have introduced the possibility of creating a binary file containing the density used to perform the calculations. This file can be easily plotted by using the program GFourier.

3. Comparison with previous results

In Ref. [1] we successfully checked the implementations done by reanalyzing FR data on 2-{3-[4-methyl-1,2,4-triazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (Metrz–Nit) reported in Ref. [5]. In this reference three sets of refinements (labeled as “A”, “B” and “C”) are presented and we checked two of them. The testing refinements in Ref. [1] were done by calculating the nuclear structure factor from the structural details in the PCR input file. With the aid of the implementations done, we have re-refined these data (in the case “B”) by using tabulated values of the nuclear structure factor read from the input data as in the original work by Gillon et al.. We have also tried to reproduce the refinement “C” by adjusting the magnetic moment in the H atoms. This leads to a considerable enhancement of the reliability factors of the refinement. The comparison between the calculated and measured FR, in

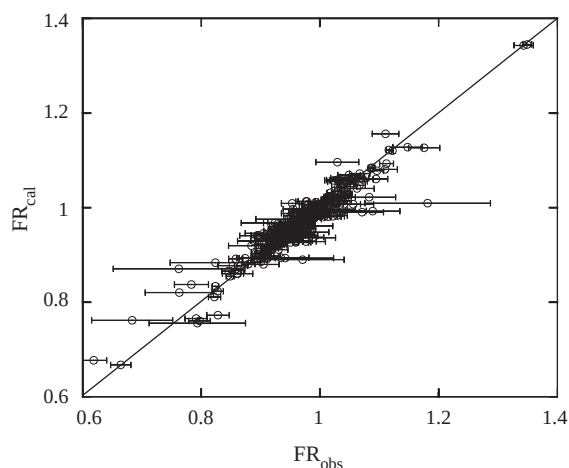


Fig. 1. Calculated vs. observed FR for Metr–Nit when considering magnetic moment in H atoms (refinement “C”).

Table 1

Comparison of results from Ref. [5] and those obtained using FULLPROF implementation on Metrz–Nit data

	2p NO approximation		2p NO + All H	
	FULLPROF	Ref. [5]	FULLPROF	Ref. [5]
R_w^{FR}	16%	16%	14%	15%
$\zeta_{\text{N}}(\text{a.u.})^{-1}$	3.80(22)	4.72(12)	4.49(25)	5.15(12)
$\zeta_{\text{O}}(\text{a.u.})^{-1}$	4.98(10)	5.44(13)	4.74(33)	5.49(13)
O1	0.219(12)	0.276(4)	0.255(12)	0.289(5)
O2	0.197(15)	0.243(5)	0.211(14)	0.243(5)
N1	−0.068(32)	0.002(5)	0.050(16)	0.011(5)
N2	−0.066(33)	−0.005(5)	−0.035(11)	−0.005(5)
N3	−0.068(33)	−0.014(4)	−0.013(10)	−0.024(5)
N4	0.230(19)	0.258(6)	0.215(18)	0.242(6)
N5	0.271(19)	0.275(6)	0.226(14)	0.276(6)
C1	0.028(15)	−0.014(6)	−0.102(24)	−0.061(7)
C2	0.033(16)	0.018(5)	−0.022(16)	0.006(6)
C3	0.018(17)	0.008(6)	0.007(16)	0.030(6)
C4	−0.064(15)	−0.084(6)	−0.038(14)	−0.081(6)
C5	0.024(13)	0.040(6)	0.050(12)	0.043(6)
C6	−0.039(18)	−0.024(7)	0.004(17)	−0.017(7)
C7	−0.013(10)	0.001(6)	−0.038(15)	−0.019(9)
C8	0.029(13)	0.008(6)	−0.004(16)	0.002(7)
C9	0.011(14)	0.006(6)	−0.028(20)	0.003(7)
C10	0.015(11)	0.005(6)	0.024(18)	0.0019(6)

The refinement has been done using tabulated nuclear structure factors provided by the authors of Ref. [5]. Table shows the agreement factors, refined Slater exponents of N and O and the refined magnetic moment of each atom normalized to $1\mu_B/\text{molecule}$. The standard deviations provided by FULLPROF are multiplied by χ^2 (approximately a factor 4).

this last case, is shown in Fig. 1. The comparative results corresponding to refinements “B” and “C”

in Ref. [5] are presented in Table 1. Both sets of results are fairly comparable ensuring the correctness of the implementations done.

We have used the implementations on hybrid s–p orbitals to check that the refinements do not significantly improve if this type of hybridization is considered in oxygen and nitrogen atoms.

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